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(54) Title: METHODS OF POSITIONS AND/OR ORIENTING NANOSTRUCTURES

(57) Abstract: Methods of positioning and orienting nanostructures, and particularly nanowires, on surfaces for subsequent use or integration. The methods utilize mask based processes alone or in combination with flow based alignment of the nanostructures to provide oriented and positioned nanostructures on surfaces. Also provided are populations of positioned and/or oriented nanostructures, devices that include populations of positioned and/or oriented nanostructures, systems for positioning and/or orienting nanostructures, and related devices, systems and methods.

METHODS OF POSITIONING AND/OR ORIENTING NANOSTRUCTURES

CROSS REFERENCE TO RELATED APPLICATIONS

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[0001] This application is related to and claims priority from and benefit of Provisional U.S. Patent Application No. 60/370,113, filed April 2, 2002, and USSN 10/239,000, filed September 10, 2002, each of which are hereby incorporated herein by reference in their entirety for all purposes.

BACKGROUND OF THE INVENTION

[0002] Nanotubes, nanocrystals, nanowires, and particularly semiconductor nanowires have gained a great deal of attention for their interesting and novel properties in electrical, chemical, optical and other applications. Such nanomaterials have a wide variety of expected and actual uses, including use as semiconductors for nanoscale electronics, optoelectronic applications in emissive devices, e.g., nanolasers, LEDs, etc., photovoltaics, and sensor applications, e.g., as nano-ChemFETS.

[0003] While commercial applications of the molecular, physical, chemical and optical properties of these materials have been postulated for all of these different types of materials, generating commercially viable products has not, as yet, been forthcoming. In the world of devices with integrated nanomaterial elements, some of the difficulties in producing commercially viable products has stemmed from the difficulty in handling and interfacing with such small scale materials. Specifically, for the most part, these materials are produced in bulk as free standing elements that must be positioned within an operational device. Accurate and reproducible positioning of these materials has proven difficult.

[0004] Accordingly, it would be desirable to be able to provide methods of positioning and orienting nanowires on substrates or within integrated devices or systems, in a reasonably practicable fashion. The present invention meets these and a variety of other needs.

SUMMARY OF THE INVENTION

[0005] The present invention is generally directed to methods of positioning and orienting nanostructures, e.g., nanowires, on substrates for subsequent use, integration or application. The invention also envisions systems for practicing such methods, devices that include oriented and positioned nanostructures, populations of positioned and/or

oriented nanostructures, and systems that include such positioned and/or oriented nanostructures.

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In one aspect, the present invention provides a method of depositing nanostructures (e.g., a nanowires) on a surface substantially in a desired orientation. The method generally comprises flowing a fluid containing nanostructures (e.g., nanowires) over the surface in a first direction, where the first direction is substantially parallel to a desired longitudinal orientation of the nanostructures (e.g., nanowires). The nanostructures (e.g., nanowires) in the solution are then permitted to become immobilized onto the surface, with the longitudinal dimension of the nanostructures (e.g., nanowires) being substantially oriented in the first direction.

In a further aspect, the invention is directed to methods of positioning nanostructures (e.g., nanowires) in one or more predetermined regions on a substrate. The methods typically comprise providing a substrate having a first surface, overlaying the first surface with a mask, where the mask provides fluid access to one or more first predetermined regions on the first surface, but not to one or more second predetermined regions on the surface of the substrate. A fluid containing nanostructures is then flowed through the mask and into contact with the first predetermined regions of the substrate surface. The nanostructures contained in the nanostructure (e.g., nanowire) containing fluid are then permitted to immobilize in the first predetermined regions of the surface of the substrate.

[0008] In another aspect, the invention is directed to one or more populations of nanostructures (e.g., nanowires) immobilized on a planar surface of a substrate, where the population(s) of nanostructures are substantially longitudinally oriented in a first direction parallel to the planar surface.

25 [0009] Similarly, the invention includes populations of nanostructures (e.g., nanowires) immobilized on a surface of a substrate that comprise a first set of nanostructures immobilized in a first selected region of the surface of the substrate, and a second set of nanostructures immobilized in a second selected region of the surface of the substrate, the second selected region being separate from the first selected region.

30 [0010] The invention is also directed to

[0010] The invention is also directed to a nanostructure (e.g., nanowire) based device that comprises at least a first population of nanostructures immobilized in at least a first region of a surface of a substrate, the first population of nanostructures being substantially longitudinally oriented in a first direction. The devices of the invention typically include at least first and second electrical contacts disposed on the first region

of the surface of the substrate. The first and second electrical contacts are typically separated from each other on the first surface of the substrate in the first direction by a less than an average length of the nanowires in the population of nanostructures.

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[0011] The invention also includes a substrate comprising a plurality of populations of nanostructures deposited upon a first surface of said substrate, wherein each of the populations of nanostructures is deposited and immobilized in a separate discrete region of the surface of the substrate. In preferred aspects, electrical contacts are disposed in the separate regions such that at least one wire in the populations of nanowires bridges and connects at least two electrical contacts.

[0012] In a further aspect, the invention is directed to a system for orienting nanostructures on a surface of a substrate in accordance with the methods of the invention. The system typically comprises a substrate having a first surface, a fluid channel disposed on the first surface, and a fluid direction system coupled to the first channel and coupled to a source of fluid containing nanostructures, for flowing the fluid containing nanowires in a first direction through the first fluid channel.

[0013] The invention also includes, as one aspect, a system for positioning nanostructures on a surface of a substrate. As above, the system includes the substrate having the first surface. A masking element is provided over the first surface which provides fluid access to separate discrete regions of the first surface of the substrate. A source of fluid that includes the nanostructures or other nanostructures is provided fluidically coupled to the fluid passages in the masking element. A fluid direction system is operably coupled to the fluid source and passages in the masking element to delver the fluid from the source to the passages, so that the nanostructures in the fluid can contact and thus be immobilized upon the discrete regions of the surface of the substrate.

In an additional embodiment, the invention provides methods of making a nanostructure device that includes a nanostructure that is embedded at at least two points in a conductive material. The methods include providing a substrate, patterning a conductive material on the substrate and patterning channels on the substrate between regions of conductive material patterned on the substrate. Nanostructures are flowed in the channels such that at least one nanostructure contacts the patterned conductive material in at least two places and an additional layer of conductive material is patterned in the at least two places, thereby providing a device comprising a nanostructure that is embedded at at least two points in a conductive material.

[0015] As with other embodiments herein, the substrate optionally includes any materials suitable to the end use application, e.g., a semiconducting crystalline material, a polymer, an amorphous surface, silicon, glass, quartz, alumina, gallium arsenide, or the like.

Optionally, the method includes growing a layer of thermal oxide on the substrate via controlled vapor deposition prior to patterning the conductive material on the substrate. Patterning the conductive material on the substrate optionally includes patterning a layer of chrome on the substrate and then patterning a layer of gold on top of the chrome. The conductive material on the substrate optionally provides conductive contact pads on the substrate.

[0017] Patterning the conductive material on the substrate optionally comprises spin coating the substrate with a negative photoresist, baking the substrate and exposing the wafer to UV through a mask. The conductive material is deposited onto the substrate in regions exposed to UV, e.g., via sputtering, organic chemical vapor deposition,

electrolysis, electrochemical deposition, or any combination thereof. For example, in one embodiment, the conductive material is sputtered onto the regions exposed to UV by first sputtering a layer of chrome onto the region and then sputtering a layer of gold onto the chrome, where the chrome is about 250 angstroms in depth and the gold is about 1000 angstroms in depth.

[0018] In one embodiment, the channels are patterned on the substrate by spin coating a positive photoresist on the substrate, baking the photoresist, exposing the substrate to UV through a mask and chemically developing the photoresist to reveal the channels. The channels can be sealed by applying a cover to an open channel structure. Flowing the nanostructures in the channels optionally includes placing a suspension of nanostructures in the channels, agitating the substrate to disperse the suspension and allowing the nanostructures to settle onto the conductive material under gravitational or centripetal force.

[0019] Patterning an additional layer of conductive material can include sputtering, organic chemical vapor deposition, electrolysis, electrochemical deposition, or any combination thereof. The additional layer of conductive material is layered on top of the nanostructure, sandwiching a portion of the nanostructure between the conductive layer and the additional conductive layer. In one specific embodiment, patterning the additional layer of conductive material comprises spin coating a negative photoresist

onto the substrate, exposing the substrate to UV light through a mask and sputtering a metal onto a region of the substrate exposed to the UV light.

[0020] It will be appreciated that nanostructure devices made by these methods are a feature of the invention. For example, a nanostructure device comprising a nanostructure embedded in at least two conductive material contact pads is a feature of the invention. For example, in one typical embodiment, the nanostructure can be a nanowire and the contact pads can comprise gold. The contact pads are optionally attached to the substrate. Systems for making the various nanostructures, as well as any or all of the structural intermediates made by the methods are also features of the invention.

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BRIEF DESCRIPTION OF THE FIGURES

- [0021] Figure 1 schematically illustrates a wafer based process for positioning and orienting nanowires on a substrate.
- [0022] Figure 2 schematically illustrates the integration of electrical elements with positioned and oriented nanowires on a wafer substrate.
 - [0023] Figure 3 is a schematic illustration of patterned substrate functionalization followed by positioning and orienting of nanowires.
 - [0024] Figure 4 shows a schematic illustration of bidirectional orientation of nanowires in accordance with the processes described herein.
- 20 [0025] Figure 5A-5D show schematic illustrations of different fluidic channel structures designed to achieve different deposition patterns of nanowires on substrate surfaces.
 - [0026] Figure 6 is a schematic illustration of an overall system for positioning and aligning nanowires onto substrate surfaces.
- 25 [0027] Figure 7 is an SEM image of oriented nanowires immobilized on a substrate surface.
 - [0028] Figure 8A is a postulated electrode deposition over the oriented nanowire population shown in Figure 7, and Figure 8B shows a plot of expected frequency of 0, 1, 2 and 3 wire connections between electrode pairs.
- Figure 9 shows aligned nanowires connected to electrical contact pairs.

DETAILED DESCRIPTION OF THE INVENTION

[0030] The present invention is generally directed to methods of positioning and/or orienting nanostructures (e.g., nanowires) on substrates, nanostructures so

positioned and/or oriented, devices produced from such oriented and/or positioned nanostructures, and systems used in so orienting and/or positioning such nanostructures.

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[0031]A "nanostructure" is a structure having at least one region or characteristic dimension with a dimension of less than 500 nm, e.g., less than 200 nm, less than 100 nm, less than 50 nm, or even less than 20 nm. In many cases, the region or characteristic dimension will be along the smallest axis of the structure. A conductive or semi-conductive nanostructure often displays 1-dimensional quantum confinement, e.g., an electron can often travel along only one dimension of the structure. Examples of nanostructures include nanowires, nanotubes, nanodots, nanorods, nanotetrapods, quantum dots, nanoribbons and the like. A "homonanostructure" is a nanostructure that has an essentially homogeneous arrangement of constituent elements. For example, a homonanowire is a homonanostructure that can be a substantially single crystal structure comprising a base material such as silicon and, optionally, a dopant dispersed in essentially the same manner throughout the crystal. A "heteronanostructure" is a nanostructure that includes subdomains comprising different compositions. For example, a heteronanowire is a heteronanostructure that can be a single crystal structure comprising a base material such as silicon with different subdomains or "segments" having different dopants, or different concentrations of one dopant, or an entirely different material, or any combination thereof. For embodiments that utilize flow alignment, the nanostructures of the invention typically have an aspect ratio greater than 5, typically greater than 10, generally greater than 50, and, optionally, greater than 100 or more.

[0032] A "nanowire" is an elongated nanostructure having at least one cross sectional dimension that is less than about 500 nm e.g., less than about 200 nm, less than about 100 nm, less than about 50 nm, or even less than about 20 nm or less, and has an aspect ratio (e.g., length:width) of greater than about 10, preferably, greater than about 50, and more preferably, greater than about 100. A nanowire is optionally substantially single crystal in structure (a "single crystal nanowire" or a "monocrystalline nanowire"). It is optionally conductive or semiconductive. A "homonanowire" is a nanowire that has an essentially homogeneous arrangement of constituent elements. For example, a homonanowire can be a single crystal structure comprising a base material such as silicon and a dopant dispersed in essentially the same manner throughout the crystal. A "heteronanowire" is a nanowire that includes subdomains comprising different compositions. For example, a heteronanowire can be a single crystal structure

comprising a base material such as silicon, with different subdomains or "segments" having different dopants, or different concentrations of one dopant, or both. Examples of nanowires include semiconductor nanowires as described in Published International Patent Application Nos. WO 02/17362, WO 02/48701, and 01/03208, carbon nanotubes, 5 and other elongated conductive or semiconductive structures of like dimensions. Particularly preferred nanowires include semiconductive nanowires, e.g., those that are comprised of semiconductor material selected from, e.g., Si, Ge, Sn, Se, Te, B, Diamond, P, B-C, B-P(BP6), B-Si, Si-C, Si-Ge, Si-Sn and Ge-Sn, SiC, BN/BP/BAs, AlN/AlP/AlAs/AlSb, GaN/GaP/GaAs/GaSb, InN/InP/InAs/InSb, BN/BP/BAs. 10 AlN/AlP/AlAs/AlSb, GaN/GaP/GaAs/GaSb, InN/InP/InAs/InSb, ZnO/ZnS/ZnSe/ZnTe, CdS/CdSe/CdTe, HgS/HgSe/HgTe, BeS/BeSe/BeTe/MgS/MgSe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbO, PbS, PbSe, PbTe, CuF, CuCl, CuBr, CuI, AgF, AgCl, AgBr, AgI, BeSiN₂, CaCN₂, ZnGeP₂, CdSnAs₂, ZnSnSb₂, CuGeP₃, CuSi2P₃, (Cu, Ag)(Al, Ga, In, Tl, Fe)(S, Se, Te)₂, Si3N₄, Ge3N₄, Al₂O₃, (Al, Ga, In)₂(S, Se, Te)₃, Al₂CO, and/or an 15 appropriate combination of two or more such semiconductors. In certain aspects, the semiconductor may comprise a dopant from a group consisting of: a p-type dopant from Group III of the periodic table; an n-type dopant from Group V of the periodic table; a ptype dopant selected from a group consisting of: B, Al and In; an n-type dopant selected from a group consisting of: P, As and Sb; a p-type dopant from Group II of the periodic 20 table; a p-type dopant selected from a group consisting of: Mg, Zn, Cd and Hg; a p-type dopant from Group IV of the periodic table; a p-type dopant selected from a group consisting of: C and Si.; or an n-type is selected from a group consisting of: Si, Ge, Sn, S, Se and Te.

order over at least 100nm in at least 1 dimension within the structure. It will be understood that a substantially single crystal nanowire may contain defects or stacking faults and still be referred to as substantially single crystal as long as long-range order is present. In addition, the surface of a nanowire can be either single crystalline, polycrystalline or amorphous without affecting the description of the overall nanowire as being substantially single crystal. In the case of a non-single crystalline surface, the nanowire is considered to be single crystal if it comprises a substantially single crystal core extending radially from the center of the wire more than 1/5 of the distance to the surface, preferably ½ of the way to the surface.

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[0034]The present invention provides for the selective deposition of nanostructures (including those noted above, e.g., nanowires) in preselected regions of substrates by providing a masking layer that masks off certain portions of the substrate surface, while providing fluid access to those portions of the substrate surface where it is desired to deposit nanostructures. Fluid containing the nanostructures is then directed through the mask such that the nanostructures contact the desired regions of the substrate, and the nanostructures are immobilized thereon. In the context of the invention, the substrate to which nanostructures are immobilized may comprise a uniform substrate, e.g., a wafer of solid material, e.g., silicon, glass, quartz, plastic, etc. or it may comprise additional elements, e.g., structural, compositional etc. For example, the substrate may include other circuit or structural elements that are part of the ultimately desired device. Particular examples of such elements include electrical circuit elements such as electrical contacts, other wires or conductive paths, including nanowires or other nanoscale conducting elements, optical and/or optoelectrical elements, e.g., lasers, LEDs, etc., structural elements, e.g., microcantilevers, pits, wells, posts, etc.

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[0035] By further controlling the direction of flow of the nanostructure containing fluid through the mask, one can substantially align or orient the nanostructures that immobilize to the surface of the substrate. For example, nanowires that are being deposited on a surface tend to be longitudinally oriented in the direction of flow of the carrier fluid in which they are suspended. Accordingly, one can substantially longitudinally orient nanowires on a surface by flowing the carrier fluid in a direction across the surface that is parallel to the desired longitudinal orientation of the nanowires. By "substantially longitudinally oriented" is meant that the longitudinal axes of a majority of nanowires or other relevant nanostructures in a collection or population of nanostructures are oriented within 30 degrees of a single direction. Preferably, at least 80% of the nanostructures in a population are so oriented, more preferably at least 90 % of the nanostructures are so oriented. In certain preferred aspects, the majority of nanostructures are oriented within 10 degrees of the desired direction.

[0036] In the context of the present invention, it is generally preferred to provide for selective positioning of nanostructures on certain regions of substrates while simultaneously providing for desired orientation of those nanostructures. However, as will be readily appreciated, there may be a number of instances in which one aspect of the invention is more desired than the other. For example, in certain cases, it may be

desired to align nanostructures on a substrate surface with little or no regard for the positioning of the nanostructures on that surface. Similarly, there may be instances where selected positioning of nanostructures is desired with little or no regard for the orientation of the nanostructures once positioned. Although the disclosure may focus a particular discussion on one aspect or the other, such discussion is generally for ease of understanding and convenience of description. It will be appreciated that in many cases, such disclosure applies equally to all aspects of the invention. Similarly, the following discussion often focuses on nanowires as an example embodiment for clarity of illustration. It will be appreciated that other nanostructures can be substituted in the methods, systems and devices, depending on the application.

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[0037] As noted previously, selective contact between nanostructures (e.g., nanowires) and regions of a substrate is accomplished through a mask-based method, where a masking element is placed over the entire substrate surface. The mask provides for fluidic access to the desired regions of the substrate. A mask may be a simple stencil type mask where a solid layer that includes apertures disposed through it is placed or fabricated over the surface of the substrate. The apertures provide the fluid access to certain regions of the substrate surface and by directing fluid containing nanostructures such as nanowires (or other collections of nanostructures, e.g., dry powders, etc.) to the surface of the substrate, one can ensure nanostructure contact, and ultimately localization and immobilization to those regions. By way of example, nanowires may be particularly targeted for positioning or localization in desired areas of the substrate, e.g., areas in which integration with additional elements is to occur, or to keep nanowires out of areas in which their presence could prove detrimental to ancillary functions of a nanowire based device. By way of example, it may be particularly desirable to ensure that nanowires contact electrical contacts or other circuit elements, while avoiding contact with other regions of the substrate surface. By doing so, one can ensure that efforts at depositing nanowires are focused in those regions of the substrate where deposition is desired, and not in other regions where it is less desirable.

In particularly preferred aspects, however, the masking element will be somewhat more complex than a simple stencil like mask. In particular, in order to provide for both positioning and orientation of nanostructures on a substrate surface, it is generally desirable to provide for directed flow of fluid across the surface of the substrate. As such, it will generally be desired to provide a masking element that provides fluidic channels across selected regions of a substrate's surface. Such masking

elements are also often referred to as manifolds. In brief, one can fabricate one or more grooves into a planar substrate to provide a manifold element. This planar element is then mated with the substrate surface upon which selective deposition of nanostructures is desired. The mating of the manifold element with the substrate surface encloses the groove on the manifold element and provides a channel which includes as one of its walls, a portion of the substrate surface. The groove typically includes a fluid inlet port and a fluid outlet port to permit the introduction and flow of fluid containing nanostructures into and through the channel in the manifold element. In more preferred aspects, these fluidic channels disposed over the substrate surface will be microscale in cross section, e.g., having a width dimension across the substrate that is less than 1 mm, preferably, less than 500 μ m, and in many cases, less than 100 μ m.

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[0039] One of the advantages of the present invention is its ability to be readily adapted to provide methods for larger scale production of nanostructure containing devices by providing full wafer scale nanostructure orientation and/or positioning processes. In particular, a nanostructure (e.g., nanowire) containing device, like most integrated circuit devices, is typically embodied in a small chip. Like the integrated circuit industry, it would be desirable to be able to manufacture multiple devices in parallel from individual and larger wafers.

[0040] In accordance with the present invention, a substrate wafer is provided from which multiple devices are to be produced. A fluid that contains nanostructures is contacted with, or in the case of flow aligned nanostructures, flowed over all or one or more selected portions of the substrate in a desired direction. As noted above, for flow aligned nanostructures, the direction of flow will typically dictate the substantial longitudinal orientation of the nanostructures that become immobilized on the surface of the substrate.

In some cases, it is preferred to provide nanostructures only on selected regions of the surface of the substrate, e.g., to minimize extraneous wire deposition, avoid wasting wires on unused portions of the substrate, etc. In such cases, a masking element is provided over the substrate surface to ensure that nanostructure containing fluid only comes into contact with one or more selected regions on the substrate surface. By way of example, a channel block or manifold that includes one or more channel grooves is placed against the substrate wafer and fluid containing the nanostructures is flowed through the channels in the desired direction to provided oriented nanostructures in the selected locations on the wafer surface.

[0042] In order to produce multiple devices from the single wafer, multiple electrical interface components are provided on the wafer. For example, in producing multiple simple devices that includes two electrical contacts bridged by one or more nanostructures, multiple pairs of electrical contacts can be provided on the substrate wafer, corresponding to each device. Typically, each pair of such electrical contacts will be provided close enough to each other in the desired direction, e.g., the direction of longitudinal orientation of the nanostructures, such that a nanostructure could bridge the space between the electrical contacts. Multiple pairs of electrical contacts are provided at multiple different positions on the wafer surface. The wafer containing multiple nanostructure devices, e.g., one or more nanowires bridging a pair of electrodes, are then segmented into multiple separate devices.

[0043] Figure 1 illustrates a wafer based process for producing nanostructure based devices. For convenience of illustration, an embodiment in which nanowires are oriented, positioned and integrated with electrical contacts for subsequent application is shown. Other nanostructures could be substituted in the device. As shown, a substrate wafer 100 is provided from which multiple nanowire based devices are to be fabricated. The wafer 100 may include surface functionalization, e.g., as described herein. A masking element, such as manifold 102 is overlaid on the relevant surface of the wafer 100. The manifold includes a plurality of fluid accesses, e.g., fluid channels 104-118, to the surface of the substrate. In particular, as shown, channels 104-118 are sealed on one side by the surface of the wafer 100, as described above. These channels are coupled to fluid ports 120 and 122 as the fluid inlet and outlet ports, respectively.

[0044] The manifold or masking element 102 may take on a variety of forms and/or be fabricated from a variety of materials. By way of example, the manifold may be fabricated from rigid substrates, e.g., glass, quartz, silicon, or other silica based materials. Such materials provide ease of manufacturing, in that the elements of the manifold, e.g., the fluidic channels, can be fabricated by processes that are well known in the microfluidics, and microfabrication industries, e.g., photolithography and wet chemical etching. Similarly, polymeric materials may be used and are readily manufactured using micromolding techniques, e.g., injection molding, microembossing, etc. In some preferred cases, flexible materials are desirable as they provide enhanced contact between the manifold element and substrate surfaces that may not be perfectly flat. Examples of such materials include, e.g., polydimethylsiloxane (PDMS) and the like. Such materials are readily produced by micromolding techniques, where molds are

fabricated in accordance with well known microfabrication techniques, e.g., photolithography and nickel electroforming of a master, followed by in situ polymerization of the PDMS manifold. Methods of fabricating such manifolds from a large variety of different materials are described in detail in the microfluidic patent literature, e.g., US Patent No., 6,180,239 to Whitesides et al, and 5,500,071 to Swedberg et al., and U.S. Patent No. 6,123,798 to Ghandi et al., the full disclosure of each of which are hereby incorporated herein by reference in their entirety for all purposes.

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[0047]

A fluid that contains nanowires is flowed into fluid inlet port 120 and through channels 104-118, and out of fluid port 122. During flow of the fluid, nanowires immobilize to the regions of the wafer surface that are included in the channels 104-118. Removal of the manifold then yields immobilized nanowire populations 124-138 in selected regions that correspond to the regions accessed by the fluid. Further, because the fluid was flowed in a selected direction, e.g., through the channels from the inlet port to the outlet port, the nanowires that are immobilized on the wafer surface in these selected regions are substantially longitudinally oriented in the direction of fluid flow, as shown by expanded view 140 which shows oriented individual wires 142.

In alternate aspects, one may employ more complex fluidic channels or [0046] fluid control systems in or attached to the manifold element to more acutely control where and how nanowires immobilize on the surface of the substrate during the deposition process. In particular, one can take advantage of fluid mechanics within the manifold channels in order to more precisely direct deposition of nanowires against a substrate surface.

Figure 5 provides examples of channel geometries or control systems that can be used to provide for wire deposition in desired locations. By way of example, Figure 5A shows a cross section of a fluidic channel 500, viewed from above where the 25 fluid channels widen at the region 502 of desired deposition. By widening the channels, fluid velocity through that channel portion is slowed (the residence time of wires in this region is increased) which enhances the likelihood that wires will deposit against the substrate in these regions, e.g., shown as the dashed oval 504. Alternatively, as shown in Figure 5B, channel regions 510 that have regions with shallower depths 512, e.g., shorter 30 diffusion distances required to be traversed to reach the substrate surface, may be provided. By providing a shorter diffusion distance between the fluid and the substrate surface region of interest, e.g., region 514, again, one may enhance the rate at which

wires contact and are deposited on the desired surface regions.

[0048] In other aspects, flow irregularities may be provided by the channel geometry which yield aggregation or deposition of particulates, e.g., nanowires, in desired regions. By way of example, and as shown in Figure 5C, one may provide channels 520 that include coves 522 in the channel geometry, or corners 524 at which will function as deposition zones 526 as a result of eddies or other recirculating flows that contain nanowires in these regions for extended times. Streamlines are indicated by the dashed arrows.

In a further aspect, one may employ other means for preferentially depositing structures such as wires in certain locations. One such example involves producing standing wave patterns in the fluid containing the nanowires over the surface of the substrate. Such standing waves can be used to create regular periodic patterns of nanowires deposited on the substrate surface. Figure 5D schematically illustrates a fluid channel 530 and wave generator 532, as well as an exemplary deposition pattern for the nanowires on the surface of the substrate. As shown, a series of standing rolls 534 is set up within a fluid containing channel that yields periodic deposition of nanowires, e.g., in zones 536. In addition, interfering waves could be set up in other directions, e.g., orthogonal to the first standing wave, to provide more precise localization of deposited wires. Wave generators that are particularly useful in accordance with this aspect of the invention include piezoelectric elements that provide high frequency vibrations to the fluid within the channel.

[0050] Positioned and oriented nanostructures such as nanowires are far more amenable to integration with electrical elements in a controlled, high yield fashion. For example, by providing populations of positioned and oriented nanowires, e.g., populations 124-138 (Figure 1), one can more precisely select locations for electrical contacts, in order to maximize the likelihood of functional connection between nanowires and electrical contacts or other elements. By way of example, if one has a population of nanowires that are randomly dispersed within a relatively small area, but are oriented to be pointing substantially in one direction, one can provide electrical contacts within that small area and spaced apart in the direction of orientation by a distance that will likely be spanned by at least one nanowire. Such a distance can be selected to be less than the average size of the nanowires in the population of nanowires. To ensure greater likelihood of spanning the contacts, one could place them at a distance that is less than 90% of the average length, less than 80% of the average length, less than 70% of the average length, and in some cases, less than 50% of the average length of the

nanowires in the population. Of course, the closer together the contacts, the more likely it becomes that one or many nanowires will bridge the two electrical contacts. Although described in terms of two electrical contacts, it will be appreciated that the nanowires may be integrated with a wide variety of other elements, including multiple, e.g., more than two electrical contacts, other circuit elements or nanoscale structures or elements fabricated into or onto the substrate (see, e.g., commonly owned Provisional U.S. Patent Application No. 60/392,205, filed June 27, 2002 and incorporated herein by reference in its entirety for all purposes), structural elements, e.g., ridges, posts, walls, etc., optical elements, or virtually any other element that would be employed in a device that comprises nanowires.

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[0051] Integration of the populations of nanostructures (e.g., nanowires) on the wafer with electrical elements can either be concurrent with the immobilization process or it can take place in a subsequent separate step. In particular, the wafer may be prepatterned with electrical contacts, such that immobilization of nanostructures in selected regions corresponding to the positions of the electrical contacts yields wires that bridge the contacts. Alternatively, the electrical contacts may be patterned over the nanostructures (or at least portions of the nanostructures) that are immobilized on the wafer.

[0052]As shown in Figure 2, a number of metallization patterns can be provided on a wafer. As shown in Figure 2, a wafer 100 that has nanowire populations 124-138 deposited thereon is subjected to further processing to deposit electrical elements onto it. As noted above, however, electrical elements may be prepatterned onto the substrate. A metallization pattern is established on the substrate using conventional photolithographic processes, e.g., photolithographically defining and developing a pattern in a resist coating over the substrate, followed by e.g., evaporative deposition or sputtering of metal electrodes in the open regions. As shown, a photomask 202 that corresponds to the desired electrode pattern 204 is used in the photolithographic definition of the electrode patterns. As can be seen, the wafer based process produces multiple discrete devices (each corresponding to a square 206 in the photomask). Once the electrodes are laid down on the substrate, the mask is removed to yield a wafer with multiple integrated devices 208, where each device includes a discrete pattern of 1 electrodes 210 that are connected by nanowires 212 within each population of nanowires. As shown, the electrode patterns are targeted to be overlaid upon the regions where the

different populations of nanowires are deposited, to maximize the potential of accurate integration of the two elements.

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[0053] As shown, the electrical contact patterns also employ elements of efficiency. In particular, as shown, a common electrode 222 is provided for all device elements-in a discrete device. In particular, while a number of nanowire based devices are provided, e.g., the wire connection between electrode 224 and 222 and between electrode 220 and 222, both elements share the common electrode 222. This permits the easier connection of the electrical contacts for all of the elements within a given device with other portions of an overall system. In the case of operable devices, it will be readily appreciated that each device may include a single wire connection or may include multiple connections, e.g., as shown in Figure 2. Further, these connections may be of the same type, e.., wires of the same composition, or with surface treatments that are the same, e.g., attached ligands, antibodies, nucleic acids, etc. (for sensor applications). Alternatively, each device may comprise multiple different wire connections, e.g., wires that have a different basic composition or surface binding element. For a discussion of sensor based applications of nanowire based devices, see, e.g., U.S. Provisional Patent Application No. 60/392,205, filed June 27, 2002, and Cui, et al., Science 293, 1289-1292 (2001), the full disclosures of which are incorporated herein by reference in their entirety for all purposes.

[0054] Again, as noted above, each metallization pattern 210 corresponds to an individual device. As shown in the expanded view, each metallization pattern 210 includes a series of patterned electrical contacts/traces, e.g., contacts/traces 220, 222, etc. The pairs of electrical contacts, e.g., contact 220 and 222, are spaced apart from each other by a distance that has a desired likelihood of having a desired number of nanowires that span the two electrical contacts. In particular, if one has a population of nanowires where the average length of nanowires is approximately $10~\mu m$, one can increase the likelihood of one or more wires spanning two electrical contacts by placing them less than $10~\mu m$ apart. The closer the electrical contacts are together, the more likely it will be that at least one nanowire sill span the two contacts. Thus, in some cases, the electrical contacts will be less than $5~\mu m$ apart, and in other cases, less than $1~\mu m$ apart.

[0055] As will be readily appreciated, the methods described herein are not limited to single sets of nanostructures (e.g., nanowires) oriented in a single direction, but can be used to provide substrates that include nanostructures oriented in any desired direction. Such differently oriented nanostructures can be positioned at different

locations on a substrate or substrate wafer, or they can be provided in the same location, e.g., layered, so as to provide arrays of crossed, but electrically or structurally coupled nanostructures. Alternatively, such layered structures may simply be used to provide a three dimensional architecture for a device, e.g., where each layer of nanostructures is separated by an intermediate layer.

[0056] For example, following immobilization and orientation of nanostructures in a first direction, the manifold element may be rotated and additional nanostructures immobilized and oriented on the surface of the substrate. The result is populations of nanostructures positioned on a substrate that are oriented in a first direction that overlap with populations of nanostructures oriented in a different direction. Nanostructures that are differently oriented may comprise the same composition or they may comprise different compositions. For example, a first population of semiconductor nanowires that is p doped may be positioned and oriented in a first direction. A second population may be positioned and oriented orthogonally to the first set and may include n-doping. The resulting p-n junction could then be used for a variety of different applications, including, e.g., optoelectronic applications, memory and logic applications, and the like, e.g., as discussed in Published PCT Application Nos. WO 02/17362, WO 02/48701, and 01/03208, the full disclosures of which are hereby incorporated herein by reference in their entirety for all purposes.

Bidirectional or multidirectional orientation of nanostructures (nanowires in this example, though it will be appreciated that other nanostructures could be substituted) is schematically illustrated in Figure 4. As shown in Figure 4, fluid containing nanowires is flowed in one direction over the substrate surface region 400 where wire deposition is desired. This results in the deposition and immobilization of wires 402 in this region where the wires are substantially longitudinally oriented in the direction of flow. Fluid containing wires are then flowed over the same substrate region 400 in a different direction, e.g., orthogonal to the original direction of flow and orientation. This results in deposition and immobilization of wires 404 on the same substrate region oriented in the different direction. This will result in a certain number of cross wire junctions 406 being formed on the substrate surface. By then adding electrical contacts 408, 410, 412 and 414, either before or after the addition of wires, one can establish integrated electrical cross junctions, which may include wires of like or different composition, e.g., doping.

[0058] In an alternative arrangement, and as discussed above, integrated nanostructure junctions may be created from a first nanostructure that is fabricated onto the surface of the substrate by more conventional means, e.g., e-beam lithography or the like (see, Provisional Application No. 60/392,205, previously incorporated herein by reference). Such "integrated circuits" may be readily combined with the free standing nanostructures in accordance with the present invention, as can other integrated circuit elements, e.g., elements that are fabricated into or onto the surface of the substrate prior to adding the nanostructure element as described in the present invention. A second nanostructure is interfaced with the first using the flow based alignment methods described herein. By way of example, a thin nanostructure element may be fabricated from an SOI wafer where the relevant semiconductor is p-doped. An n-doped, free standing nanostructure is then deposited across the first wire element to provide a p-n junction. A variety of different junction types may be created in this manner, including simple switches, etc. as described above.

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- 15 [0059] As described above, the methods of the invention involve the immobilization of nanostructures onto a surface of a substrate. As used herein, the term "immobilization" refers to the coupling of a nanostructure with the substrate surface, or chemical groups on that surface, such that the nanostructure remains in position on the substrate surface despite being contacted by fluids, moving air or gas, etc.
- Immobilization may be permanent or reversible. Typically, immobilization is the result of chemical interaction between the surface or chemical groups on the surface and the nanostructures themselves, or chemical groups on the nanostructures. Such interactions include, e.g., ionic interactions, covalent interactions, hydrophobic or hydrophilic interactions, and electrostatic or magnetic interactions.
- In the case of certain substrates and nanostructures, the existing surfaces of the substrate and the nanostructure may provide sufficient attraction between the substrate and the nanostructure to provide immobilization. For example, where the nanostructures and substrate surface are generally hydrophilic, one could dispose the nanostructures in a hydrophobic solvent to contact them with the surface. As a result, the favored reaction would be for the nanostructures to associate with the substrate surface, resulting in immobilization. Alternatively, and in particularly preferred aspects, one may provide surface functionalization on one or both of the substrate and/or the nanostructure that facilitates coupling between the two.

[0061]In functionalizing the substrate surface, where such functionalization is necessary or desired, one may provide the ability to couple the nanostructures to an entire substrate surface and rely upon the masking step to selectively position nanostructures, or one may also provide only selected regions of functionalized surfaces to further selectively position nanostructures on the surface. In particular, one may 5 functionalize only first selected regions on the substrate or wafer. Then, by masking off other selected regions that include portions of the functionalized regions, one can further control how nanostructures are coupled to the surface of the substrate. Figure 3 illustrates such a process using the same manifold 102 for surface functionalization followed by nanostructure deposition. As shown, manifold 102 is placed over wafer 10 100, and appropriate functionalization chemistry is directed through the channels of the manifold. This results in derivatized surface regions that correspond to channels 104-118. The manifold is then rotated, e.g., 90°, and nanostructure containing fluid is directed through the manifold. Because only a portion of the surface which the nanostructures contact is functionalized, the nanostructures will be positioned and oriented substantially only in those regions. When the manifold is removed, it yields a substrate in which nanostructures are only immobilized in selected small regions, e.g., regions 324, 326, etc., that were both functionalized, and exposed to nanostructures. This provides for even more precise control over positioning of the wires. For example, one can target the functionalization to provide more precise localization of nanostructures in the desired regions, such as functionalizing the surface of the electrical contacts, but no other portions of the substrate surface, in order to assure that the wires immobilize only to the electrical contacts, or in the regions where electrical contacts are to be provided.

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[0062] Functionalization of the surface may be carried out by any of a variety of means. For example, as discussed above, functionalization may be directed at an entire substrate surface, or it may be patterned or chemically templated onto the substrate surface. As used herein, the term "chemical template" generally refers to the deposition and/or reaction upon a substrate surface of a template that is defined by chemical modification of that substrate surface. In particular, chemical modification of the surface in selected regions will make it more likely that a nanostructure will localize to a particular region, e.g., a desired region, than in another region, e.g., an undesired region. Chemical modification can be positive modification, e.g., the region of modification provides enhanced affinity of the nanostructure to the substrate, or it can be negative,

e.g., it provides a repulsing effect such that nanostructures are unlikely to localize in the particular region. Chemical modifications include any of a variety of different surface treatments that are well known in the art of surface chemistry, including coupling of active groups that are capable of bonding to or otherwise associating with the nanostructures or with chemical groups disposed upon those nanostructures. The functional chemical groups presented may interact with the nanostructures via affinity interactions, ionic interactions, hydrophobic and/or hydrophilic interactions.

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[0063] As noted above, the substrate may comprise a bare substrate or may include other elements, including other device elements and/or other nanostructures, e.g., electrodes, nanostructures, circuit elements, etc. The chemical moieties may be an element of the substrate, or they may be coupled, either directly or through a linker molecule, or otherwise provided upon the surface of the substrate in the desired pattern or at the desired locations or regions of the substrate's surface.

[0064] One arrangement for capturing nanostructures involves forming surfaces that comprise regions that selectively attract nanostructures. For example, -NH₂ moieties can be presented in a particular pattern at a surface, and that pattern will attract nanowires or nanotubes having surface functionality attractive to amines. This same surface functionality is also optionally used to generate an ionic attraction whereby surface amines are exposed to an acidic environment resulting in a predominantly positively charged surface, e.g., populated with NH₃⁺ groups that can attract negatively charged nanostructure surfaces or repel like charged materials. Surfaces can be patterned using known techniques such as electron-beam patterning, soft-lithography, or the like. See also, International Patent Publication No. WO 96/29629, published July 26, 1996, and U.S. Patent No. 5, 512,131, issued April 30, 1996.

[0065] Templates may have inherent affinity toward nanostructures, or may be provided such that the affinity can be accentuated. For example, in preferred aspects, chemical templates are generated by providing protected functional groups over the surface of the substrate upon which the nanostructures are going to be provided. Desired portions or regions of the substrate surface are then deprotected, e.g., the protecting groups are removed or transformed, to yield an active site to which nanostructures will bind or otherwise be localized. As alluded to above, the regions of the substrate that are deprotected may comprise a basic substrate surface, e.g., a SiO₂ substrate, or they may include other elements, including functional elements, on the surface of a basic substrate. For example, a chemical template may define regions only on the surfaces of electrical

contacts that are present on a basic substrate, and not elsewhere on the substrate surface, so as to increase the likelihood that nanostructures, e.g., nanowire(s), will be coupled to those electrodes, and nowhere else.

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In a first aspect, photodeprotection is used to provide a chemical template [0066] for directed positioning of nanostructures. In particular, a substrate to which nanostructures are to be coupled, bound or otherwise associated, is treated to provide a layer of chemical moieties that include active functional chemical groups that would interact, e.g., bind, to a nanostructure, but for the presence of a protecting group coupled to that active group. In accordance with this aspect of the invention, the protecting group provided on the active group is a photolabile protecting group. Specifically, in order to activate the molecules on the surface of the substrate, one must expose the photolabile protecting group to light of a desired wavelength, to remove the protecting group and yield the active chemical moiety with which a nanostructure may interact/bind. By selectively exposing desired regions of the substrate, one can selectively activate a pattern of regions on that surface and drive the selective positioning of nanostructures accordingly. Such selective exposure can be carried out using standard photolithographic techniques, e.g., mask-based exposure, laser writing, e-beam lithography, etc. that are very well known in the art.

[0067] A wide variety of photolabile protecting groups and their associated linkage chemistries, e.g., that couple other elements to surfaces, once activated, are well known in the art, and have been used extensively in the directed positioning of chemical elements on substrate surfaces. By way of example, in at least one aspect of the invention, amino or hydroxyl terminated organosilane linker molecules are provided coupled to the substrate surface. The linker group is capped by a protecting group that is cleaved or rendered cleavable upon exposure to light of a desired wavelength. Examples of known photolabile protecting groups include nitroveratryloxycarbonyl protecting groups, such as NVOC and MeNVOC, as well as nitropiperonyloxycarbonyl protecting groups, such as NPOC and MeNPOC, and others, e.g., PyMOC. The use of these protecting groups and others in photolithographic activation of surfaces is described in, e.g., U.S. Patent Nos. 5,489,678 and 6,147,205, the complete disclosures of which are hereby incorporated herein by reference in their entirety for all purposes.

[0068] In alternative arrangements, functional groups may be in an ionizable form, such that under certain conditions, e.g., low or high pH, the functional group has substantial affinity for the nanostructure, e.g., a strong positive or negative charge, while

under different environmental conditions, the affinity is substantially lower, or is even negative.

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[0069] In certain aspects, the organosilane polymer is terminated with a hydrophilic moiety. In such cases, the natural affinity of the nanostructure components, e.g., for semiconductor nanowires, to the hydrophilic moiety provides the selectivity of binding in the overall positioning process. Examples of linkers including such hydrophilic terminators include, e.g., (hydroxy/amino) propyltriethoxy silane derivatives and poly(hydroxy/amino)propyltriethoxysilane derivatives. To take advantage of an increase in hydrophilicity, protecting groups for this particular embodiment would be generally hydrophobic in nature. Cleavage would then yield an increase in hydrophobic surface templates has been described for use in, e.g., in situ chemical synthesis for biochemical microarrays (see, e.g., U.S. Patent No. 5,985,551, to Brennan et al.).

[0070] In this case, following exposure of the desired regions to expose the hydrophilic moiety in the desired regions for coupling nanostructures, a fluidic suspension of nanostructures is flowed over or otherwise contacted with the entire substrate. The affinity of the nanostructures, e.g., semiconductor nanostructures, for the hydrophilic regions provides for the preferential localization of the nanostructures in the deprotected regions. Such regions may include regions between and including electrical contacts, or between electrical contact(s) and other nanostructures, or regions on substrates where subsequent additional elements will be patterned to contact the nanostructures so deposited.

[0071] While described in terms of hydrophilic affinity, it will be appreciated that a variety of different interactions may be exploited in the attraction and/or repulsion of nanostructures within the selected pattern, including hydrophobic interactions, e.g., in regions where it is not desired to have binding, combined hydrophobic/hydrophilic interactions, specific molecular affinity interactions, e.g., antibody:antigen, aviden:biotin, nucleic acid hybridization, or ionic interactions.

[0072] In the cases of affinity interactions (and even in other non-affinity cases, where higher efficiency coupling is desired), it may be necessary or desirable to provide a functional group on the nanostructure to permit the desired interaction between the nanostructure and the substrate, e.g., a complementary molecule to that disposed on the substrate surface. In such cases, and particularly with reference to semiconductor nanowires, e.g., silicon nanowires, derivatization of the nanowire may be carried out

according to methods used to derivatize the substrate surface of like make-up. For example, nanowires may be silanized for attachment to the substrate surface, either directly or through an intermediate group. In particular, in the same fashion described for derivatizing the surface of the substrate, supra, one could derivatize the nanowire itself. Such derivatization could include addition of affinity molecules, hydrophilic or hydrophobic groups, ionic groups, etc. as desired to improve efficiency of the positioning process. In addition, functionalization of the nanowire provides facility in adding additional components to the nanowire element, i.e., for attachment of biomolecules for biosensor applications (see, e.g., U.S. Patent Application No. 60/392,205, previously incorporated herein). Thus, in certain cases both the nanowire and substrate may be derivatized to facilitate binding and improve efficiency of the positioning process.

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above, patterning of a surface for nanostructure attachment may utilize chemical deprotection methods, e.g., acid deprotection. Acid deprotection generally utilizes acid labile protecting groups in place of the photolabile protecting groups described above. Directed exposure of regions to acid may be accomplished through mechanically directed means, e.g., channeling acid to the desired regions while preventing the acid from reaching other regions. Such mechanical means can include the use of channel blocks mated with the substrate, template masks. However, such methods often yield low resolution due to the difficulty in sealing the channel block to the substrate surface. Other mechanical methods include ink jet printing methods, microcontact printing methods, etc.

[0074] For modification of electrodes to increase affinity, one could provide the patterned electrodes with a thin gold layer as the chemical moiety to increase affinity, and treat the nanostructures with thiol terminated organosilanes. The thiolated nanostructure would then bind preferentially to the gold electrode.

[0075] Alternatively, photoresist layers are used to generate a mechanical stencil or mask for subsequent acid exposure. In particular, a resist is coated on a substrate that includes acid labile protecting group capping the functional groups. The resist is exposed and developed, e.g., removed, in the desired regions and the exposed portions of the substrate are subjected to acid deprotection while the unexposed regions are not. In still more preferred aspects, an acid generating resist is used, where exposure of the resist in the desired locations results in generation of an acid which in turn deprotects the functional groups in those desired locations. This latter method has an added advantage

of reducing the number of required process steps, in that the exposure and acid deprotection steps are concurrent.

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[0076]Examples of both acid labile protecting groups and acid generating photoresists are well known in the art and include, e.g., DMT (dimethoxytrityl) and its derivatives, as well as acid generating resist layers that are generally commercially available.

[0077]Although described primarily in terms of photolithographic patterning techniques, it will be appreciated that other patterning techniques, such as microcontact printing techniques, laser ablative techniques (either direct or in conjunction with a resist layer, i.e., PMMA), and the like may be employed in the patterning steps. Such methods are generally well known in the art and are described in, e.g., U.S. Patent Nos. 6,180,239 to Whitesides et al, and 5,500,071 to Swedberg et al.

[0078]For other applications, different protecting group types may be employed, e.g., allyloxycarbonyl (ALLOC), fluorenylmethoxycarbonyl (FMOC), --NH-FMOC groups, t-butyl esters, t-butyl ethers, and the like. Various exemplary protecting groups are described in, for example, Atherton et al., (1989) Solid Phase Peptide Synthesis, IRL Press, and Greene, et al. (1991) Protective Groups In Organic Chemistry, 2nd Ed., John Wiley & Sons, New York, N.Y.

For the steps of selectively patterning nanostructures onto the surface, 20 through the use of a masking element, while in preferred aspects, the masking element or manifold is provided as a separate element or layer that is removably placed against the substrate surface, it will be appreciated that this element may be fabricated onto the surface of the substrate, e.g., in the same fashion as described with reference to chemical templating of the substrate surface. Further, this masking element may remain 25 permanently on the surface of the substrate, or it may be removed through subsequent processing of the substrate. In particular, a manifold element may be fabricated onto a substrate or substrate wafer surface by coating a layer of material, e.g., a polymeric resist layer on the substrate. In preferred aspects, polymeric resists, and preferably photoresists are spin coated onto wafer surfaces. As described above, the substrate may include 30 electrical contacts pre-patterned onto the surface of the wafer. Similarly, the surface may be pre-functionalized in first selected regions for coupling to nanostructures, as described above.

[0800] Following coating of the layer that is to form the manifold or masking layer onto the substrate surface, passages are defined through that layer, typically as

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troughs, trenches or fluid channels in the layer to provide fluid access to the surface of the substrate. By using a photoresist as the masking layer, one can simply use the recommended exposure and development processes for the resist used to define the passages. Once the masking layer is defined on the surface of the substrate, fluid containing the nanostructures is flowed over the substrate and/or specifically through the defined channels or troughs in the desired direction in order to allow the nanostructures to be immobilized on the substrate surface in the desired orientation. As will be appreciated, enclosed or sealed channels are generally preferred for flowing nanostructures in a desired direction. As such, in preferred aspects, an additional cover layer is optionally and preferably disposed over the masking layer to provide flow channels, like with a manifold. While either positive or negative resists may generally be employed in accordance with the invention, for use in templating, it will be generally desirable to use positive photoresists, as they are less prone to swelling in aqueous solutions or in ethanol, which is often employed as the fluid carrier for nanostructures, e.g., nanowires. Positive resists additionally provide better adhesion to many substrate layer types, e.g., silicon, and provide greater mechanical strength. This allows for more precise templating or masking in the positioning of nanostructures. As noted, this layer may be removed in subsequent steps or it may be allowed to remain on the overall device to provide additional structural features, e.g., insulation, moisture barriers, fluidic conduits, etc. A wide variety of different positive and negative resists are generally commercially available, e.g., from DuPont, i.e., DuPont 8000 series resists. Once the nanostructures are deposited, the masking layer may be removed

from the substrate to allow for additional processing. Alternatively, where various integration elements are prepositioned on the wafer or substrate, it may not be necessary to remove the masking layer. In fact, in some cases, the masking layer may provide a barrier or insulation between electrical or fluidic elements of a device. In the case of such masking layers, it will be appreciated that any of a variety of resist layers are readily commercially available for this process, including, e.g., polyimide or PMMA based resists, or any of a variety of resists that are generally commercially available.

[0082] One of the advantages of the invention is its applicability to manufacturing on a commercial scale. In accordance with this advantage, Figure 6 schematically illustrates an overall system that may be used in commercial scale alignment and deposition of nanowires onto substrates and subsequent device integration (it will be appreciated that other nanostructures could be used in place of the nanowires,

in certain variant applications). As shown, the system 600 includes a source of nanowire containing fluid 602. A pump 604 delivers the fluid to the inlet port 606 of a deposition module 608 which would typically include a base substrate 610 onto which nanowires are to be deposited, and a manifold element 612 which directs the flowing nanowires to selected regions on the surface of the substrate to which the manifold is mated. Following contact with the substrate, the fluid exits the manifold 612 through outlet port 614, where the fluid and the nanowires still contained therein are reclaimed, e.g., in a reclamation vessel (not shown) or recycled back into source 602 (as shown). Typically, the module 606 may be multiplexed either in parallel, e.g., as shown by module 616, or in series, as shown by module 618, provided there is a sufficient concentration of nanowires in the fluid, in order to increase the throughput of the deposition process.

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EXAMPLES

[0083] Example 1: Controlled Positioning and Flow Alignment of Nanowires
on a Wafer Scale

15 [0084] Nanowires were positioned and oriented on a substrate and subsequently integrated with electrical connections in accordance with the invention.

[0085] Silicon nanowires used for flow alignment were synthesized by gold cluster mediated chemical vapor deposition methods, and the resulting nanowires were suspended in ethanol solution via ultrasonication.

In [0086] A poly(dimethylsiloxane) (PDMS) stamp, e.g., as shown in Figure 1, was fabricated by photolithography. The PDMS stamp had a three-inch diameter, with eight parallel channels spaced 7 mm apart with each channel having a width of 500 μ m, and a depth of ~200 μ m.

[0087] A silicon substrate wafer (surface oxidized, 600 nm oxide) to be used in flow assembly was functionalized with an NH₂-terminated self-assembled monolayer (SAM) by immersion in a 1 mM chloroform solution of 3-aminopropyltriethoxysilane (APTES) for 30 min, followed by heating at 110°C for 10 min.

[0088] Alignment of nanowires was performed by conforming the PDMS stamp to the functionalized surface of the silicon substrate. The ethanol solution of nanowires was flowed into the parallel channels of the stamp through one port (inlet) and out through the other port. Flow was either induced by gravity, e.g., tilting the substrate to $\sim 40^{\circ}$, or through application of a positive pressure to the inlet port.

[0089] Once the nanowire solution was delivered through the stamp, the PDMS stamp was removed, and the surface of the substrate wafer was coated with a photoresist.

Figure 7 shows an SEM image of flow aligned nanowires immobilized on a substrate. As can be seen, a substantial majority of the nanowires are substantially longitudinally oriented in a single direction in the direction of flow during the deposition process.

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[0090] By superimposing virtual or postulated pairs of electrical contacts over the oriented nanowires, one can estimate the efficacy of the fabrication process in producing functioning nanowire containing devices, e.g., devices in which one or more nanowires connects a pair of electrical contacts. A virtual electrical contact pattern overlaid on the oriented nanowires is shown in Figure 8A. Examination of overlay in Figure 8A allows for an estimate of 0, 1, 2 and 3 wire connections between electrode pairs. Figure 8B provides a plot of the distribution of connections in the estimated devices of Figure 8A. As can be seen, functional device yield, e.g., percentage of devices showing one or more connection between a pair of electrical contacts, is approximately 75%.

[0091] Photolithography was used to selectively remove portions of the photoresist, and electron-beam evaporation was performed to define the metal contacts on to the nanowires in selected locations on the substrate surface. The pattern of electrodes was as shown in Figure 1. Figure 9 illustrates the overall device, as well as expanded views of the electrodes and nanowire connections between electrode pairs. Electrode pairs are made up between the common central electrode and each of the separate orthogonally oriented electrodes. Each connected electrode pair, e.g., connection between the central electrode and an orthogonal electrode, represents an operation element of a nanowire based device.

[0092] Example 2: Nanostructure Manufacturing Process

[0093] This example relates to a method of making a nanostructure device, as well as to devices produced by the methods and systems for making the devices. In the methods, a substrate (e.g., including a semiconducting crystalline material, a polymer, an amorphous surface, silicon, glass, quartz, alumina, and/or gallium arsenide) is provided. A conductive material is patterned onto the substrate. This can be performed, e.g., by spin coating the substrate with a negative photoresist, baking the substrate, exposing the wafer to UV through a mask, and, depositing the conductive material onto the substrate in regions exposed to UV, via sputtering, organic chemical vapor deposition, electrolysis, electrochemical deposition, or any combination thereof. For example, in one embodiment, the methods includes growing a layer of thermal oxide on the substrate via controlled vapor deposition and patterning the conductive material on the substrate, e.g.,

by layering gold over chrome. This conductive material can include any features useful for interfacing with the nanostructures, e.g., providing contact pads that link the nanostructures to other electronic elements of the device.

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[0094] Channels are patterned on the substrate between regions of conductive material patterned on the substrate. Here too, patterning the channels on the substrate can include any typical process for patterning channels on a substrate, e.g., spin coating a positive photoresist on the substrate, baking the photoresist, exposing the substrate to UV through a mask and chemically developing the photoresist to reveal the channels. Alternately, machining methods can be used. The channels can be open topped, or sealed by applying an appropriate cover layer to the channels. In either case, nanostructures are flowed in the channels such that at least one nanostructure contacts the patterned conductive material in at least two places. This process can include, e.g., placing a suspension of nanostructures in the channels, agitating the substrate to disperse the suspension and allowing the nanostructures to settle onto the conductive material under gravitational or centripetal force.

[0095] An additional layer of conductive material is patterned in the at least two places, providing a device comprising a nanostructure that is embedded at at least two points in a conductive material. This process also can include, e.g., sputtering, organic chemical vapor deposition, electrolysis, electrochemical deposition, or any combination thereof, whereby the additional layer of conductive material is layered on top of the nanostructure, sandwiching a potion of the nanostructure between the conductive layer and the additional conducive layer. For example, this process can include comprises spin coating a negative photoresist onto the substrate, exposing the substrate to UV light through a mask and sputtering a metal onto a region of the substrate that was exposed to the UV light.

standard semiconductor manufacturing equipment to enhance the manufacturability and scalability of the process. Any of a number of different substrates can be used as described above, e.g., silicon, glass, gallium arsenide, or the like. The following process is an example for the purpose of illustrating the manufacturing process of the nanowire device. The example device consists of silicon wafer as a substrate, on to which a 1 micron layer of thermal oxide is grown via chemical vapor deposition. A patterned layer of chrome and fold is formed on the wafer, via a process of spin coating a wafer, with negative photoresist, baking the photoresist and exposing the wafer to UV light which

has traveled through a mask. A positive photoresist could be used in this application, provided the photomask is changed to compensate for the different chemical reaction process in the photoresist. The photoresist patterning process opens up areas into which metal can be deposited in subsequent steps.

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[0097] Next, a layer of chrome 250 Angstroms deep is sputter deposited into the open areas of the wafer. This is followed by a sputtering of 1000 Angstrom of gold on top of the chrome. The metal layers can also be deposited in any of a number of different ways, including, e.g., sputtering, metal organic chemical vapor deposition, electrolysis and/or electrochemical deposition. The photoresist defining the metal containing wells is stripped away using the appropriate organic solvent. This results in the contact pads and wires. A layer of positive photoresist is spin coated on the wafer. The photoresist is baked to remove the solvent and promote the adhesion between the organic photoresist and the underlying layer. The wafer is exposed using a contact aligner and a photomask. After the development of the photoresist using the appropriate chemicals, narrow channels are revealed. The channels located in the center of the nanowire device, are for the placement of nanowires which become incorporated in the nanowire device.

[0098]Trenches located toward the side of the structure can be used as test patterns. These channels are for testing the placement and alignment of the nanowires. To place the nanowires on the metal contact areas located in the center of the structure, a suspension of nanowires in ethanol is placed on the photoresist. The wafer is agitated to evenly disperse the suspension into the channels where the nanowires settle under gravitational force. The nanowires which settle on the contact pad will adhere to the pads while the nanowires which settle on the silicon dioxide do not adhere. After a given amount of time, the solution of ethanol containing the nanowire is removed and the wafer is rinsed with ethanol to remove the nanowires which settle on the silicon dioxide. The photoresist which defined the fluid channels is removed using the appropriate solvent. A new layer of negative photoresist is spin coated on the wafer. The wafer is baked to remove the solvent and promote the adhesion between the organic photoresist and the underlying layer. The photoresist is exposed to ultraviolet light which has traveled through a photomask to open up metal contact areas. The photoresist is developed via the appropriate developing chemicals to reveal unmasked areas located around the point where a nanowire contacts a nanowire contact pad. Metal is sputtered

over the wafer to fill the nanowire contact pads. The photoresist is removed using the appropriate solvent to reveal a metal blanket surrounding the nanowire.

[0099] Although described in considerable detail above, it will be appreciated that various modifications may be made to the above-described invention, while still practicing the invention as it is delineated in the appended claims. All publications, patents patent applications or other documents cited herein are hereby incorporated herein by reference in their entirety for all purposes to the same extent as if each such document was individually indicated to be incorporated for all purposes herein.

WHAT IS CLAIMED IS:

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1	1. A method of depositing a population of nanostructures on a surface
2	substantially in a desired orientation, comprising:
3	flowing a first fluid containing nanostructures over the surface in a first direction
4	the first direction being parallel to a desired longitudinal orientation of the
5	nanostructures; and
6	permitting a population of nanostructures in the first fluid to become
7	immobilized onto the surface, a longitudinal dimension of the nanostructures from the
8	first fluid being substantially oriented in the first direction.

- 1 2. The method of claim 1, wherein the flowing step comprises providing a 2 microscale fluid channel on the surface of the substrate and flowing the first fluid 3 through the fluid conduit in the first direction.
- 1 3. The method of claim 1, comprising providing a plurality of fluid channels 2 over different regions of the surface of the substrate, and flowing the first fluid through 3 each of the fluid conduits in the first direction.
 - 4. The method of claim 2, wherein the microscale fluid channel comprises one or more of a widened region, a shallow region, and a cove, the nanostructures preferentially immobilizing in the one or more widened region, shallow region and cove.
- The method of claim 2, wherein the step of providing a microscale fluid channel on the substrate surface comprises providing a manifold having a first groove disposed in its first surface, and mating the first surface of the manifold with the surface of the substrate to define a first enclosed channel on the first surface of the substrate.
 - 6. The method of claim 2, wherein the step of providing a microscale fluid channel on the substrate surface comprises providing a layer of polymeric material on the substrate surface and defining the microscale fluid channel in the layer of polymeric material to provide fluidic communication to at least a portion of the substrate surface.

7. The method of claim 6, wherein the layer of polymeric material comprises a photoresist, and the step of defining the microscale fluidic channel comprises exposing a portion of the layer of photoresist and developing the layer of photoresist to define the microscale fluidic channel.

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- 8. The method of claim 6, further comprising providing a cover layer over the layer of polymeric material to seal and enclose the microscale fluidic channel, the cover layer comprising at least a first port disposed therethrough and positioned to provide fluid access to the microscale fluidic channel.
- 1 9. The method of claim 8, wherein the photoresist comprises a positive 2 photoresist.
- 1 10. The method of claim 1, wherein the permitting step comprises providing 2 the first surface of the substrate as a functionalized first surface that is capable of binding 3 the nanostructures from the first fluid.
- 1 11. The method of claim 10, wherein the step of providing the first surface of 2 the substrate as a functionalized first surface comprises providing functional groups on 3 only a portion of the first surface.
- 1 12. The method of claim 11, wherein the portion of the first surface comprises 2 one or more electrical contacts.
- 1 13. The method of claim 11, wherein the functional groups comprise 2 protectable or deprotectable functional groups.
 - 14. The method of claim 13, wherein the functional groups comprise photodeprotectable functional groups.
- 1 15. The method of claim 1, further comprising the step of providing at least 2 first and second electrical contacts on the surface of the substrate, the first and second 3 electrical contacts being separated by a first distance in the first direction on the first

4 substrate, the first distance being less than an average length of the nanostructures in the

- 5 first fluid containing nanostructures.
- 1 16. The method of claim 15, wherein the first and second electrical contacts
- 2 are provided on the surface of the substrate before flowing the fluid containing the
- 3 nanostructures over the first surface.
- 1 17. The method of claim 15, wherein the first and second electrical contacts 2 are provided on the surface of the substrate after the nanostructures have been permitted
- 3 to be immobilized on the first surface of the substrate.
- 1 18. The method of claim 1, further comprising flowing a second fluid 2 containing nanostructures over the surface in a second direction different from the first
- 3 direction, and permitting the nanostructures in the second fluid to become immobilized
- 4 onto the surface whereby a longitudinal dimension of the nanostructures from the second
- 5 fluid being substantially oriented in the second direction.
- I 19. The method of claim 18, wherein the nanostructures from the first fluid 2 oriented substantially longitudinally in the first direction are immobilized to at least a
- 3 portion of a same region of the surface of the substrate as nanostructures from the second
- 4 fluid oriented substantially longitudinally in the second direction.
- 1 20. The method of claim 18, wherein the nanostructures from the first fluid
- 2 oriented substantially longitudinally in the first direction are immobilized to a different
- 3 region of the surface of the substrate as nanostructures from the second fluid oriented
- 4 substantially longitudinally in the second direction.
- 1 21. The method of claim 1, further comprising:
- functionalizing at least a first portion of the surface of the substrate, prior to
- 3 flowing the first fluid containing the nanostructures over the first surface in the first
- 4 direction, whereby the nanostructures immobilize to the first portion of the surface of the
- 5 substrate that has been functionalized.

1 The method of claim 21, wherein the first fluid is flowed over a second 22. 2 portion of the surface of the substrate, the first portion of the surface and the second 3 portion of the surface at least partially overlapping. 1 23. The method of claim 21, wherein the first surface of the substrate 2 comprises at least one other circuit element to which nanostructures are to be coupled. 1 24. The method of claim 23, wherein the at least one other circuit element 2 comprises at least a first pair of electrical contacts. 1 25. The method of claim 24, wherein the first pair of electrical contacts 2 comprises first and second metal contact regions on the surface of the substrate. 1 26. The method of claim 23, wherein the at least one other circuit element 2 comprises a nanowire circuit element 1 27. The method of claim 26, wherein the nanowire circuit element comprises 2 doping different from doping in the nanowires in the first fluid. 1 28. The method of claim 23, wherein the circuit element comprises an 2 integrated circuit element disposed on the substrate. 1 29. The method of claim 18, wherein the integrated circuit element comprises 2 a nanoscale circuit element. 1 30. A method of positioning nanostructures in one or more predetermined 2 regions on a substrate, comprising: 3 providing a substrate having a first surface; 4 overlaying the first surface with a mask, the mask providing fluid access to one or more first predetermined regions on the first surface, but not to one or more 5 6 second predetermined regions on the surface of the substrate; flowing fluid containing nanostructures through the mask and into contact

with the first predetermined regions of the substrate surface; and

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permitting the nanostructures contained in the nanostructure containing fluid to immobilize in the first predetermined regions of the surface of the substrate.

- 1 31. The method of claim 30, wherein the step of providing the substrate 2 comprising the first surface comprises providing the first surface as a functionalized 3 surface capable of binding to the nanostructures.
- 1 32. The method of claim 30, wherein the flowing step comprises flowing the 2 fluid containing the nanostructures over the first predetermined regions in a first 3 direction to cause the nanostructures to immobilize in the first predetermined regions on 4 the surface of the substrate longitudinally oriented substantially in the first direction.
 - 33. The method of claim 30, further comprising providing at least first and second electrical contacts in the one or more first predetermined regions, whereby one or more nanostructures immobilize in contact with both the first and second electrical contacts in the first predetermined region.

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- 1 34. The method of claim 33, wherein the first and second electrical contacts 2 are provided in the first predetermined regions of the substrate before the nanostructures 3 are immobilized in the first predetermined regions.
 - 35. The method of claim 33, wherein the first and second electrical contacts are provided in the first predetermined regions of the substrate after the nanostructures are immobilized in the first predetermined regions.
 - 36. A population of nanostructures immobilized on a planar surface of a substrate, the population of nanostructures being substantially longitudinally oriented in a first direction parallel to the planar surface.
- The population of nanostructures of claim 36, comprising a plurality of discrete sets of nanostructures immobilized on separate regions of the surface of the first substrate, the nanostructures in each separate region being substantially longitudinally oriented in a selected direction.

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38. The population of nanostructures of claim 36, wherein the first substrate at least first and second electrical contacts disposed thereon, the first and second contacts being positioned sufficiently proximal to each other in the first direction, such that at least one nanostructure in the population of nanostructures is simultaneously contacting both of the first and second electrical contacts.

- 1 39. The population of nanostructures of claim 38, wherein the first and 2 second electrical contacts are deposited over at least a portion of the at least one 3 nanostructure.
- 40. 1 A population of nanostructures immobilized on a surface of a substrate, 2 comprising:
- 3 a first set of nanostructures immobilized in a first selected region of the 4 surface of the substrate; and
- 5 a second set of nanostructures immobilized in a second selected region of the surface of the substrate, the second selected region being separate from the first selected region.
 - 41. A nanostructure based device, comprising:

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- 2 at least a first population of nanostructures immobilized in at least a first 3 region of a surface of a substrate, the first population of nanostructures being substantially longitudinally oriented in a first direction; 4
 - at least first and second electrical contacts disposed on the first region of the surface of the substrate; and
- 7 wherein the first and second electrical contacts are separated from each 8 other on the first surface of the substrate in the first direction by a less than an average 9 length of the nanostructures in the first population of nanostructures.
- 42. 1 The nanostructure based device of claim 41, wherein at least one 2 nanostructure in the population of nanostructures is positioned in contact with both the 3 first and second electrical contacts.

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1 The nanostructure based device of claim 41, wherein the first and second 43. 2 electrical contacts are separated by a distance that is less than 90% of the average length 3 of nanostructures in the first population of nanostructures.

- 1 The nanostructure based device of claim 41, wherein the first and second 44. electrical contacts are separated by a distance that is less than 80% of the average length 2 of nanostructures in the first population of nanostructures. 3
- 1 The nanostructure based device of claim 41, wherein the first and second 45. 2 electrical contacts are separated by a distance that is less than 50% of the average length 3 of nanostructures in the first population of nanostructures.
- 1 The nanostructure based device of claim 45, wherein the first and second 46. electrical contacts are separated by a distance that is less than 10 μm . 2
- 1 The nanostructure based device of claim 46, wherein the first and second 47. 2 electrical contacts are separated by a distance that is less than 1 μ m.
- The nanostructure based device of claim 46, further comprising at least 1 48. third and fourth electrical contacts separate from the first and second electrical contacts, 2 and disposed on the first region of the first surface, wherein the third and fourth electrical 3 contacts are separated from each other on the first surface of the substrate in the first 4 direction by less than an average length of the nanostructures in the population of 5 nanostructures.

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The nanostructure based device of claim 46, further comprising: 49. at least a second population of nanostructures immobilized in at least a second region of the surface of the substrate, the second population of nanostructures being substantially longitudinally oriented in a second direction; at least third and fourth electrical contacts disposed on the second region of the surface of the substrate; and wherein the third and fourth electrical contacts are separated from each other on the first surface of the substrate in the second direction by a less than a 1

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9 μ m/distance that is less than an average length of the nanostructures in the population of nanostructures.

1	of claim 46, further comprising:
2	at least a second population of nanostructures immobilized in at least a
3	second region of the surface of the substrate, the second population of nanostructures
4	being substantially longitudinally oriented in a second direction;
5	at least third and fourth electrical contacts separate from the first and
6	second electrical contacts, and disposed on he first region of the first surface, wherein the
7	third and fourth electrical contacts are separated from each other on the first surface of
8	the substrate in the first direction by less than (1 μ m/a distance that is less than an
9	average length of the nanostructures in the first population of nanostructures); and
10	at least fifth and sixth electrical contacts disposed on the second region of
11	the surface of the substrate, wherein the fifth and sixth electrical contacts are separated
12	from each other on the first surface of the substrate in the second direction by a less than
13	(1 μ m/distance that is less than an average length of the nanostructures in the second
14	population of nanostructures).

51. A substrate comprising

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- 2 a plurality of populations of nanostructures deposited upon a first surface 3 of said substrate; and
- wherein each of the populations of nanostructures is deposited and immobilized in a separate discrete region of the surface of the substrate.
 - 52. The substrate of claim 51, further comprising at least a first pair of electrical contacts deposited on the surface of the substrate, the first pair of electrical contacts being positioned to be in electrical contact with wires in at least a first of the plurality of nanostructure populations.
- 1 53. A system for orienting nanostructures on a surface of a substrate, 2 comprising:
- a substrate having a first surface;
- a fluid channel disposed on the first surface; and

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a fluid direction system coupled to the first channel and coupled to a source of fluid containing nanostructures, for flowing the fluid containing nanostructures in a first direction through the first fluid channel.

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- 1 54. The system of claim 53, wherein the fluid channel is defined in a first 2 surface of a manifold, the first surface of the manifold being mated to the first surface of 3 the substrate to dispose the fluid channel on the first surface of the substrate.
- 1 55. The system of claim 54, further comprising at least a second fluid channel 2 disposed on the first surface of the substrate.
- 1 56. The system of claim 55, wherein the first and second fluid channels are 2 fluidly coupled to a first fluid inlet port, the first fluid inlet port being fluidly coupled to 3 the source of fluid containing nanostructures.
- 1 57. A system for positioning nanostructures on a substrate, comprising: 2 a substrate having a first surface; 3 a masking element disposed over the first surface and providing one or 4 more fluid passages to one or more discrete regions of the first surface; 5 a source of fluid containing nanostructures fluidly coupled to the one or 6 more fluid passages on the masking element; and a fluid direction system for delivering fluid from the fluid source to the 7 8 one or more fluid passages.
 - 58. The system of claim 57, wherein the masking element comprises a manifold having a plurality of fluid channels disposed therein, the plurality of fluid channels having as at least one wall of the one or more fluid channels the one or more regions of the surface of the substrate, the fluid channels providing the one or more fluid passages to the first surface of the substrate.
- 59. The system of claim 58, wherein one or more of the fluid channels 2 comprises a widened region corresponding to a position on the surface of the substrate where it is desired to position nanostructures, the widened region providing longer

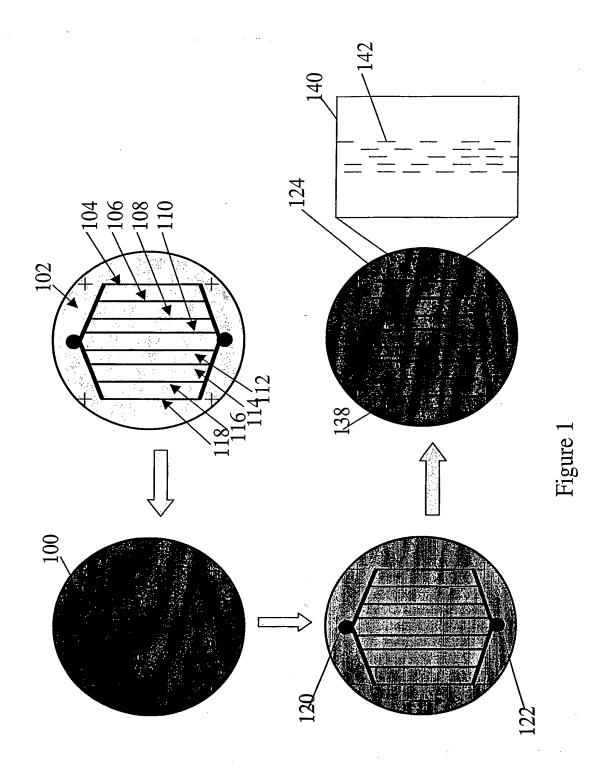
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4 residence time within the wider region for a fluid flowing through the one or more fluid

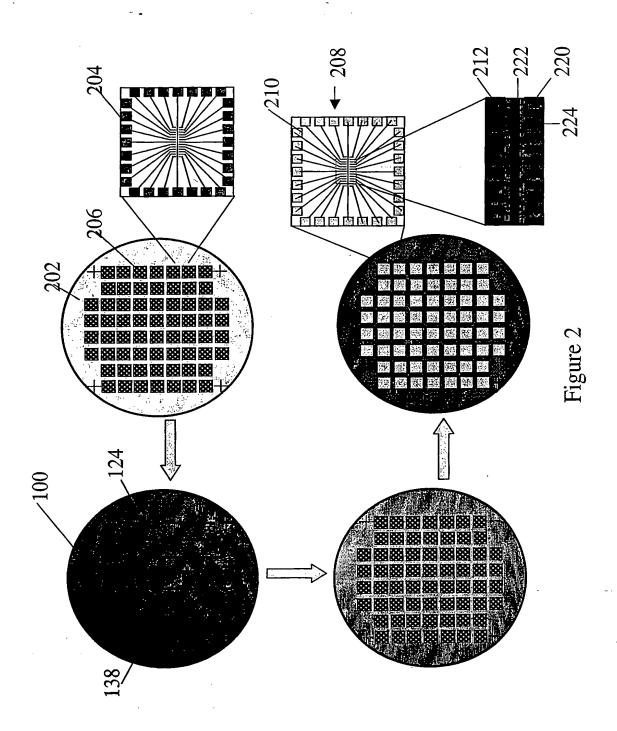
- 5 channels.
- 1 60. The system of claim 58, wherein the one or more fluid channels
- 2 comprises a thinned region that provides a shorter average diffusion distance between a
- 3 fluid flowing through the thinned region of the one or more channels and the surface of
- 4 the substrate at the thinned region of the one or more fluid channels.
- 1 61. The system of claim 58, wherein the manifold comprises a flexible
- 2 material.
- 1 62. The system of claim 61, wherein the flexible material comprises a
- 2 polymeric material.
- 1 63. The system of claim 61, wherein the flexible material comprises PDMS.
- 1 64. A method of positioning nanostructures on a surface of a substrate,
- 2 comprising:

- 3 contacting the surface of the substrate with a fluid containing the
- 4 nanostructures;
- 5 establishing a standing wave through the fluid, the standing wave
- 6 localizing nanostructures preferentially in first selected-regions of the surface of the
- 7 substrate and not in second selected regions of the substrate.

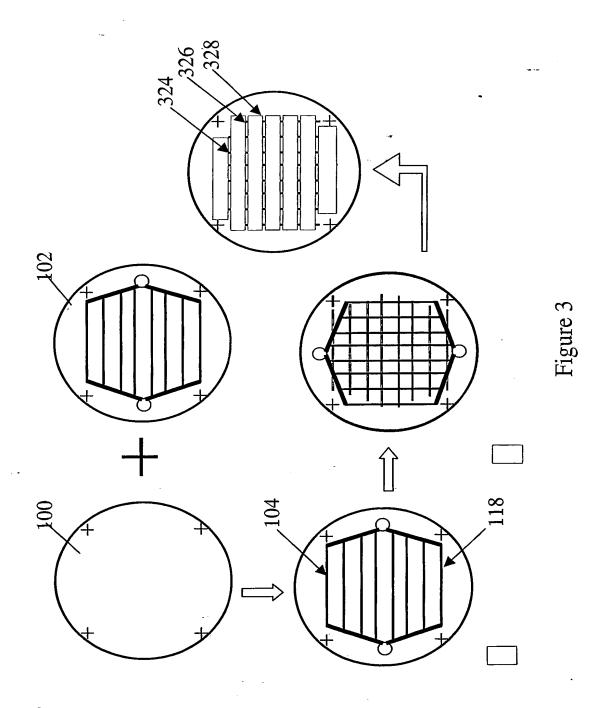
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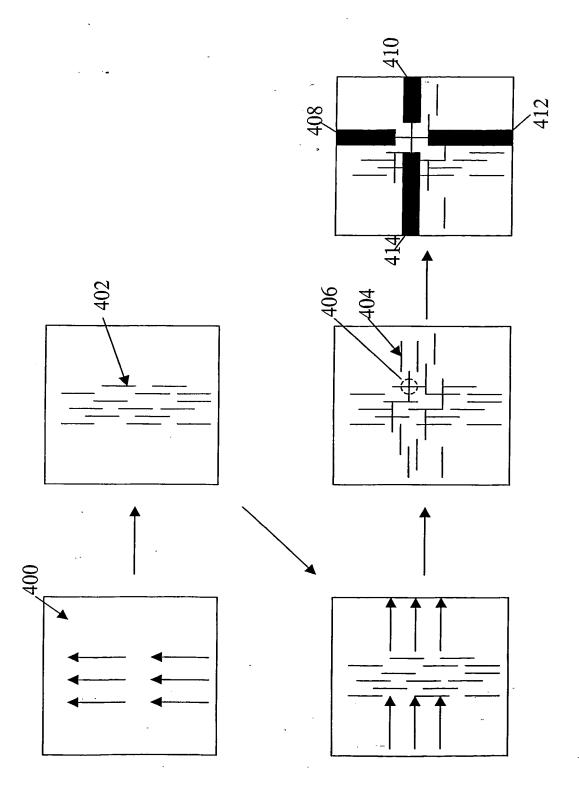
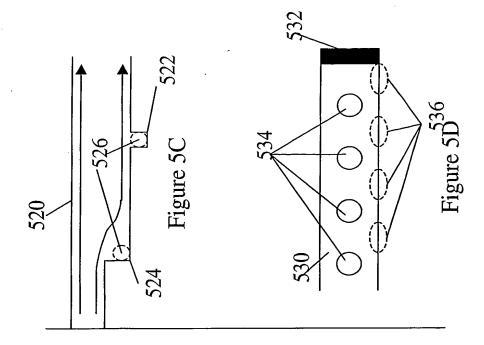
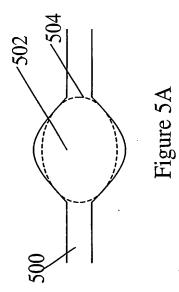
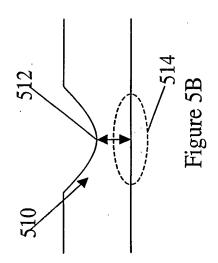


Figure 4

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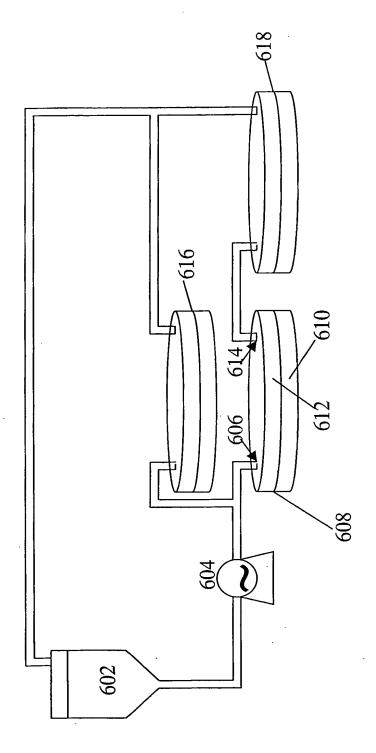


Figure 6

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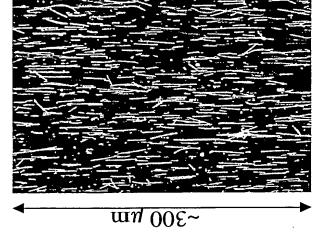


Figure 7

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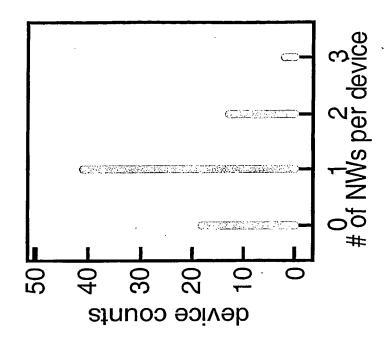


Figure 8B

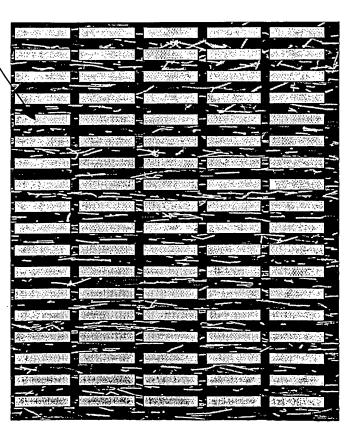


Figure 8A



